Supporting information

Defect-Controlled Electronic Structure and Phase Stability in Thermoelectric Skutterudite $CoSb_3$

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The additional remarks in our calculation

In our previous intrinsic defect study of $CoSb_3$,[1] we did a *k*-points test. In the supercell (256 atoms) calculation of $CoSb_3$, the formation energy of neutral defect Co_i in the Co rich region with a 2×2×2 Gamma-centered *k*-points sampling was 1.20 eV, which is only 0.06 eV lower than that (1.26 eV) with a Gamma only *k*-points sampling. Thus, the Gamma only *k*-points sampling is sufficient for our supercell calculation.

In the supercell (256 atoms), the free energy of the neutral $O_{i\text{-}7}$ structure is 2.71 eV lower than that of the $O_{i\text{-}v}$ structure. In the cubic unit cell (32 atoms), the energy difference between these two neutral structures is 2.79 eV, as shown in the main text. Our test results indicate that the energy difference between $O_{i\text{-}7}$ and $O_{i\text{-}v}$ sites is robust when increasing the supercell size.

Our calculations reveal that S (or Se) and Te will not bond together, as shown in Figure 3(c) and 3(e). The atomic distance of S–Te and Se–Te is 3.697 and 3.310 Å, respectively. In the S_i + Te_{Sb} structure with S and Te as the nearest neighbor, the initial atomic distance of S–Te is ~3.301 Å. We think S and Te will not bond together after relaxation. Thus, this is the similar case as shown in Figure S3(b). So we didn't consider this structure.

For complex defect of single atom *M* doped $CoSb_3$, there are so many different combinations such as $M_i + M_{Sb}$, $2M_{Sb}$ as shown in Figure S2(a) below, $2M_i + M_{Sb}$, $3M_i + M_{Sb}$, $4M_i + M_{Sb}$, $4M_i + 2M_{Sb}$, and so on.[2] For different *M* atoms, there are much more possibilities. This requires a large number of dedicated calculations, which we will consider in our future studies.

The PBE functional has been shown to be reliable for calculating various properties of $CoSb_3$, which is carefully discussed in our intrinsic defect study of $CoSb_3$.[1]

Initial single point defect structures for the three types of defects in *M* (*M* = O, S, Se, Te) doped Co_8Sb_{24}

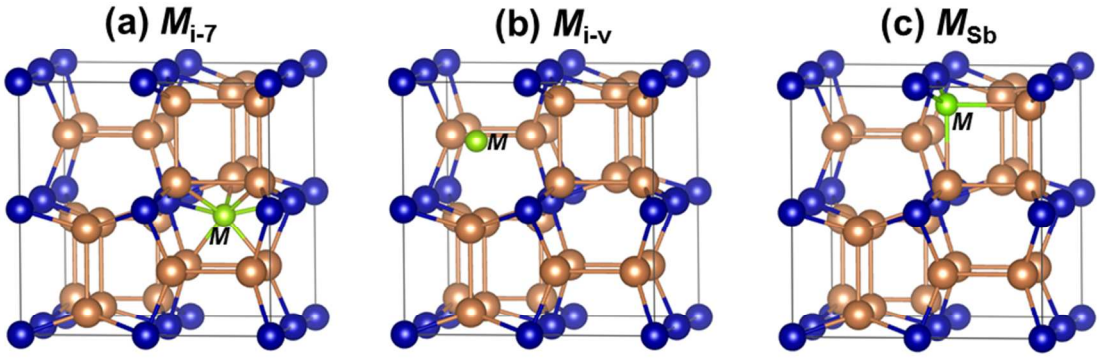

Figure S1. Initial single point defect structures for the three types of defects in *M* (*M* = O, S, Se, Te) doped Co_8Sb_{24}: (a) *M* interstitial with 7-fold coordination, M_{i-7}; (b) *M* interstitial in the void center, M_{i-v}; (c) *M* substituting Sb, M_{Sb}. The *M* atom is represented with the green color. For O interstitial (O_i), the neutral O_{i-7} structure has a lower free energy than the neutral O_{i-v} structure after relaxation. TheO_{i-7} structure is chosen for the charged defect formation energy calculation. For the interstitial of *M* (M_i, *M* = S, Se, Te), the neutral M_{i-v} structure has a lower free energy than the neutral M_{i-7} structure. Thus, the O_{i-7} and M_{i-v} (*M* = S, Se, Te), structures are chosen for the charged defect formation energy calculations.

Initial local atomic structure of neutral S_{Sb}+Te_{Sb} complex defect in S and Te co-doped $Co_{64}Sb_{192}$

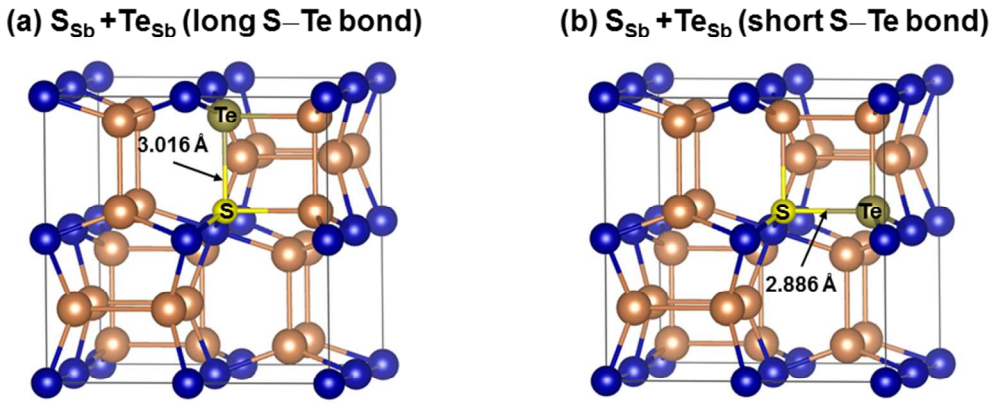

Figure S2. Initial local atomic structure of neutral S_{Sb}+Te_{Sb} complex defect in S and Te co-doped $Co_{64}Sb_{192}$. (a) The S_{Sb}+Te_{Sb} structure with the long S–Te bond length of 3.016 Å. (b) The S_{Sb}+Te_{Sb} structure with the short S–Te bond length of 2.886 Å. The S and Te atoms are represented with the yellow and brown colors, respectively. After relaxation, the free energy of the structure (a) is 0.356 eV lower than that of the structure (b), representing the structure (a) is more stable than the structure (b). Thus, the S_{Sb}+Te_{Sb} structure with the long S–Te bond length are chosen to perform the charged defect formation energy calculations.

Initial local atomic structure of neutral S_i+Te_{Sb} complex defect in S and Te co-doped $Co_{64}Sb_{192}$

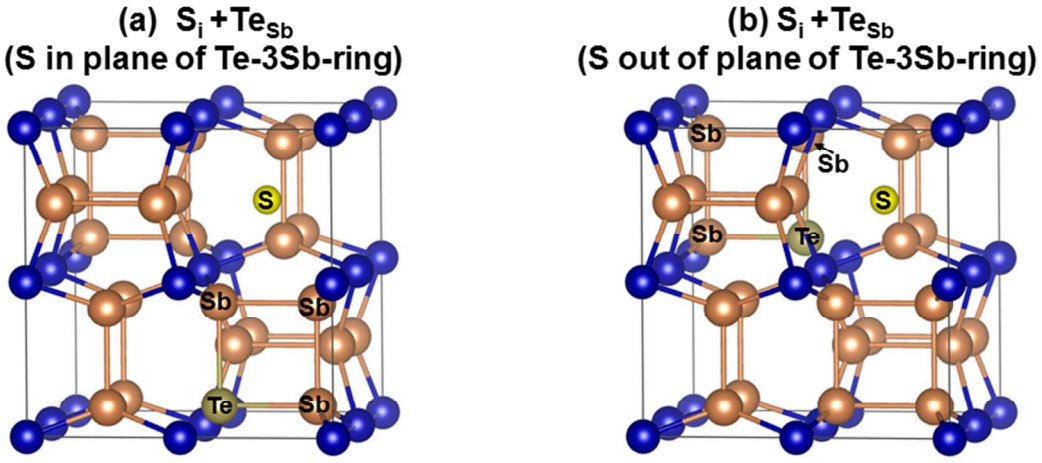

Figure S3. Initial local atomic structure of neutral S_i+Te_{Sb} complex defect in S and Te co-doped $Co_{64}Sb_{192}$. (a) The S_i+Te_{Sb} structure with the S filler atom in plane of the Te-3Sb-ring. (b) The S_i+Te_{Sb} structure with the S filler atom out of plane of the Te-3Sb-ring. The S and Te atoms are represented with the yellow and brown colors, respectively. After relaxation, the free energy of the structure (a) is 0.351 eV lower than that of the structure (b), representing the structure (a) is more stable than the structure (b). Thus, the S_i+Te_{Sb} structure with the S filler atom in plane of the Te-3Sb-ring are chosen to perform the charged defect formation energy calculations.

REFERENCES

(1) Li, G.; Bajaj, S.; Aydemir, U.; Hao, S.; Xiao, H.; Goddard, W. A.; Zhai, P.; Zhang, Q.; Snyder, G. J., p-Type Co Interstitial Defects in Thermoelectric Skutterudite $CoSb_3$ Due to the Breakage of Sb_4-Rings. *Chem. Mater.* **2016,** 28, 2172-2179.

(2) Xi, L.; Qiu, Y.; Zheng, S.; Shi, X.; Yang, J.; Chen, L.; Singh, D. J.; Yang, J.; Zhang, W., Complex Doping of Group 13 Elements In and Ga in Caged Skutterudite $CoSb_3$. *Acta. Mater.* **2015**, 85, 112-121.